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Published in:
Journal of Molecular Structure

DOI:
10.1016/S0022-2860(96)09522-1

Publication date:
1997

ELSEVIER

Journal of Molecular Structure 408/409 (1997) 499–505

Journal of
MOLECULAR
STRUCTURE

IR spectroscopic investigations into reactions between unsaturated titanium complexes and CO or N_2 in liquid xenon or heptane

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Received 26 August 1996; accepted 6 September 1996

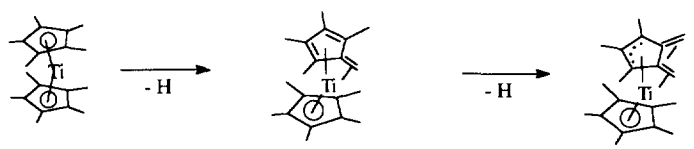
Abstract

The reactions of Cp^*_2TiR compounds with CO in liquid xenon (LXe) or heptane were studied by IR spectroscopy in special high-pressure cells. All complexes incorporate a single CO molecule to fill up their coordination sphere, forming $Cp^*_2TiR(CO)$ intermediates. These species undergo secondary reactions at elevated temperatures, such as disproportionation to Ti(II) and Ti(IV) complexes. The formation of the 18 VE species $Cp^*_2Ti(CO)_2$ seems to be the driving force of the observed reactions. A similar behavior was found in the reaction of Cp^*_2TiH with dinitrogen, where the adduct $Cp^*_2TiH(N_2)$ and its $^{14/15}N_2$ isotopomer was identified together with $Cp^*_2Ti(N_2)_2$. In addition to these orientating experiments, the stable 15 VE Cp^*FvTi (Fv = η_6–$C_5Me_4CH_2$) and 16 VE species Cp^*AdTi (Ad = η_7–$C_5Me_3(CH_2)_2$) show the addition of carbon monoxide to form new, reactive titanium carbonyls, which undergo ligand exchange reactions at higher temperatures and form $Cp^*_2Ti(CO)_2$ as one of the final products. © 1997 Elsevier Science B.V.

Keywords: IR spectroscopy; Liquid xenon; Titanium complexes

1. Introduction

Cp^*_2TiR compounds [1] are well-known subcoordinated 15 valence electron systems, both electronically and sterically stabilized by Cp^* ligands. Loss of one or two hydrogen atoms from one Cp^* ligand leads to similarly stable 15 or 16 valence electron species, Cp^*FvTi and Cp^*AdTi [2]:



Cp*2Ti Cp*FvTi Cp*AdTi

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PII S0022-2860(96)09522-1

In this article we present an infrared spectroscopy study of the primary steps of the reaction between CO and the complexes Cp^*_2TiR (R = H, Me, Ph, O^{t}Bu), Cp^*FvTi and Cp^*AdTi. In addition, the reactions between N_2 and both Cp^*_2TiH and Cp^*_2TiMe have been studied. The reaction of permethyl titanocene, Cp^*_2Ti [3], with CO or N_2 is well documented, as is the CO-induced disproportionation under elevated pressure of the halide complexes Cp^*_2TiX (X = Cl, Br, I) [4] and of $(Cp_2TiCl)_2$ [5], proceeding through monocarbonyl adducts. However, there are no reports of the CO adducts of the very reactive Cp^*_2TiR, nor of Cp^*FvTi or Cp^*AdTi.

$$2Cp^*_2TiCl \overset{p<90\ \text{bar CO}}{\underset{\text{toluene}}{\rightleftarrows}} 2Cp^*_2Ti(Cl)(CO)$$

$$\overset{\text{disprop}}{\longrightarrow} Cp^*_2Ti(CO)_2 + Cp^*_2TiCl_2$$

In order to obtain reaction conditions for the observation of reactive intermediates, cold inert solvents (liquid xenon and heptane) were used. Experimental difficulties involved with the paramagnetic nature of most compounds were avoided by employing IR rather than NMR spectroscopy. Although liquid xenon (LXe) is a more ideal solvent because of its complete IR transparency, heptane provides a higher solubility for the complexes, which increases the accessible temperature range significantly. The combination of the results of both solvents allowed for the characterization of a series of new thermolabile titanium carbonyls and the detection of some secondary reaction products.

2. Experimental

The starting materials Cp^*_2TiCl (**Ia**) [6], Cp^*_2TiH (**Ib**) [1], Cp^*_2TiMe (**Ic**) [1], Cp^*_2TiPh (**Id**) [1], $Cp^*_2TiO^tBu$ (**Ie**) [6], Cp^*TiCHT (CHT = cycloheptatriene = C_7H_7) (**II**) [7], Cp^*FvTi (**III**) [2] and Cp^*AdTi (**IV**) [2] were prepared according to literature methods. High purity gases Xe (4.5; Air Products), CO (4.7; AGA), ^{13}CO (99.8% ^{13}C, 14.8% ^{18}O; Matheson) and N_2 (5.2; AGA) were used as purchased. Heptane (Merck–Schuchard) was distilled from sodium potassium alloy and stored under nitrogen.

In a typical LXe experiment, about 0.5 mg compound together with a magnetic stirring bar were placed in the LXe cell under a flow of xenon (details of the cell have been published elsewhere [8]). Subsequently, the cell was cooled down to 173 K and filled with 4.5 ml of liquid xenon. The solution was stirred until the concentration reached a maximum. Spectra of the starting compound were recorded on a Bio-Rad FT–IR spectrometer (4000–1000 cm^{-1}, 32 scans, resolution 2 cm^{-1}). While the cell was still positioned in the IR spectrometer, it was pressurized with 1 bar CO containing the natural ratio of ^{12}CO to ^{13}CO, unless stated otherwise. Approximately 1/2 min later the first spectrum was obtained. The carbonyl intermediate was allowed to form its maximum concentration before being characterized by IR spectroscopy. If the ^{13}CO satellite was not observable, the experiment was carried out with ^{13}C and ^{18}CO enriched carbon monoxide. Subsequent reactions were monitored by IR spectroscopy by warming the solution in steps of 10 K up to the maximum temperature of 243 K.

These experiments were also carried in a low-temperature IR liquid cell with free access to the reaction volume (LT-FAIR cell) [8], unless stated otherwise. Here, a 0.01–0.1 M solution of the parent compound in heptane was injected into the cell which was cooled to 188 K under a nitrogen atmosphere in an Oxford Instruments XL-500 cryostat. At this temperature a stream of CO was passed through the solution for about 10 min until saturation was reached. The spectroscopic investigations were carried out in the same way as in the LXe experiments.

3. Results

*3.1. Cp^*_2TiR (R = Cl (**Ia**), H (**Ib**), Me (**Ic**), Ph (**Id**), O^{t}Bu (**Ie**))*

In the presence of CO all parent compounds are transformed into monocarbonyl adducts $Cp^*_2TiR(CO)$ (eqn (1)). The species were found to be thermolabile and undergo consecutive reactions, which are not observed for the donor free complexes:

$$2Cp^*_2TiR \overset{+CO}{\underset{LXe}{\rightarrow}} 2Cp^*_2Ti(R)CO \overset{\Delta}{\underset{LXe}{\rightarrow}} \text{further reactions} \quad (1)$$

Table 1
CO stretching frequencies of $Cp^*_2Ti(R)(CO)$ isotopomers and their thermal stabilities in LXe

Parent compound	ν(CO) ($Cp^*_2Ti(R)(CO)$ (cm^{-1})			Stable up to (K)
	$\nu(^{12}C^{16}O)$	$\nu(^{13}C^{16}O)$	$\nu(^{13}C^{18}O)$	
Cp^*_2TiCl **Ia**[a]	2014	–	–	243
$Cp^*_2TiO^tBu$ **Ie**	1997	1953	1924	183
Cp^*_2TiH **Ib**[b]	1967	1924	–[c]	203
Cp^*_2TiPh **Id**	1963	1919	–	223
Cp^*_2TiMe **Ic**	1957	1914	–	243[d]

[a] Data from [4].
[b] ν(TiH) = 1497 cm^{-1}.
[c] ν(TiH) = 1561 cm^{-1}.
[d] T_{max} of LXe cell.

The thermal stability of the carbonyl adducts depends on the ligand R; it increases in the order of $Cp^*_2TiO^tBu(CO)$ < $Cp^*_2TiH(CO)$ < $Cp^*_2TiPh(CO)$ < $Cp^*_2TiCl(CO)$ < $Cp^*_2TiMe(CO)$. In the case of R = H, O^tBu and Ph, the secondary reaction product $Cp^*_2Ti(CO)_2$ was formed and easily detected by IR spectroscopy (ν(CO) = 1940, 1860 cm^{-1}). The CO stretching frequencies and other characteristic properties are listed in Table 1.

The corresponding reaction products formed by CO-induced disproportionation, such as the expected $Cp^*_2TiR_2$, could not be observed due to the lack of characteristic IR frequencies and possibly because of their poor solubility in LXe. Fig. 1 shows the IR spectrum in the (CO) region of the products formed when a solution of Cp^*_2TiH (**Ib**) and CO in LXe is raised in temperature. While the adduct band of $Cp^*_2TiH(CO)$ at 1967 cm^{-1} decreases in time, the

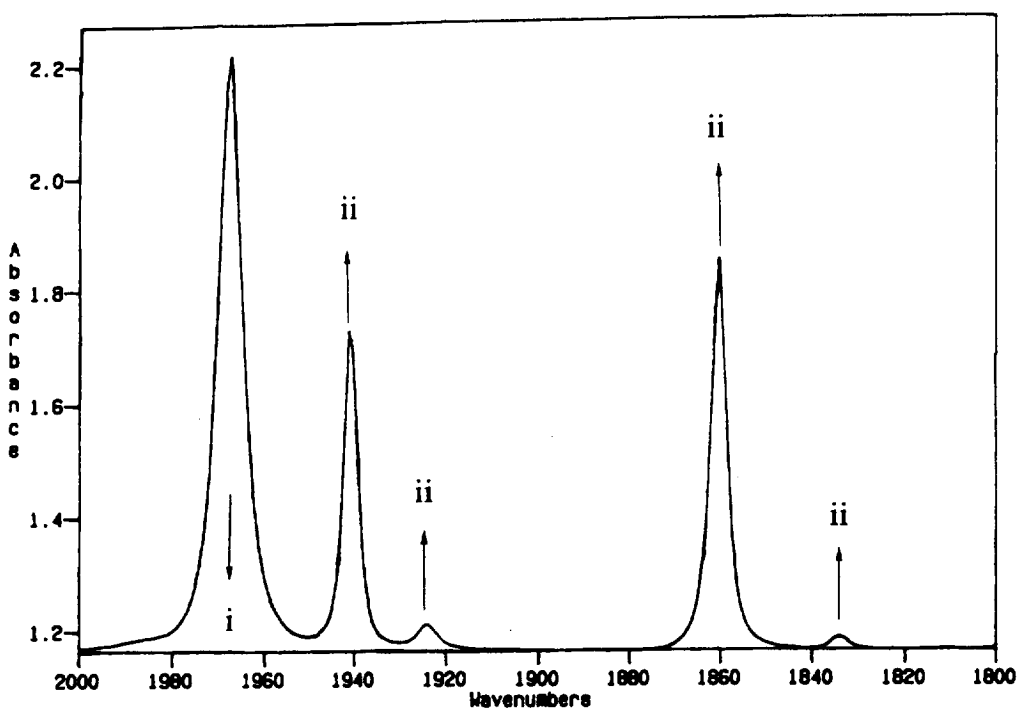


Fig. 1. IR spectral changes in the (CO) stretching region of Cp^*_2TiH + 1 bar CO in LXe upon warming up from 173 to 243 K: (i) $Cp^*_2Ti(H)(CO)$; (ii) $Cp^*_2Ti(CO)_2$.

bands at 1940 and 1860 cm^{-1} and their respective ^{13}C satellites increase simultaneously. The latter belong to the dicarbonyl, $Cp^*_2Ti(CO)_2$, which is therefore postulated as the reaction product. Under the same conditions, the alkyl derivative, $Cp^*_2TiMe(CO)$, is stable up to 243 K in LXe with no evidence for disproportionation or CO insertion.

Because of the limited temperature range dictated by the vapour pressure of LXe, all experiments (except that of **Ie**) were also performed in an LT-FAIR cell [8], filled with a solution of the parent compound in heptane. In this solvent the formation of the monocarbonyls, $Cp^*_2TiR(CO)$, can also be detected. However, the thermal stability of the adducts $Cp^*_2TiPh(CO)$ and $Cp^*_2TiMe(CO)$ is less than in LXe. On raising the temperature (233 K), new absorption bands were obtained for both compounds; these are attributed to CO insertion products in the Ti–C bond (titanium acyls). This reaction appears to be complex [9] and so far not all products could be identified unambiguously by IR spectroscopy. An in-depth study of this will be published later. **Ib** behaved in heptane the same way as in LXe.

Because of their coordinative unsaturation and high affinity to CO, complexes **Ib** and **Ic** were expected to react with the less reactive N_2 as well. Applying a 3 bar N_2 pressure to a solution of **Ib** in LXe at 173 K gave evidence for the formation of a dinitrogen adduct $Cp^*_2TiH(N_2)$ with $(N_2) = 2143\ cm^{-1}$ and $(TiH) = 1513\ cm^{-1}$. Its concentration was sufficiently high to observe its $^{14/15}N_2$ satellite ($\nu(^{14/15}N_2) = 2108\ cm^{-1}$). Warming up to 243 K resulted in a decrease of the band at 2143 cm^{-1}, while two new absorptions showed up at 2088 and 1980 cm^{-1} respectively. These bands are assigned to the bis-dinitrogen complex $Cp^*_2Ti(N_2)_2$ (Fig. 2). A dinuclear titanium complex with a bridging dinitrogen ligand such as $Cp^*_2Ti(N_2)(\mu_2\text{–}N_2)(Cp^*_2Ti(N_2)$ [3] can be excluded: for that the symmetric and antisymmetric dinitrogen stretching frequencies should differ only in a few wavenumbers, unlike what was observed. A similar experiment performed with **Ic** under identical conditions did not provide a mono- or bis-dinitrogen complex, which demonstrates the reduced affinity to dinitrogen of **Ic** in comparison with **Ib**.

The above-mentioned formation of $Cp^*_2Ti(N_2)_2$ appears to be catalysed by a small amount of CO.

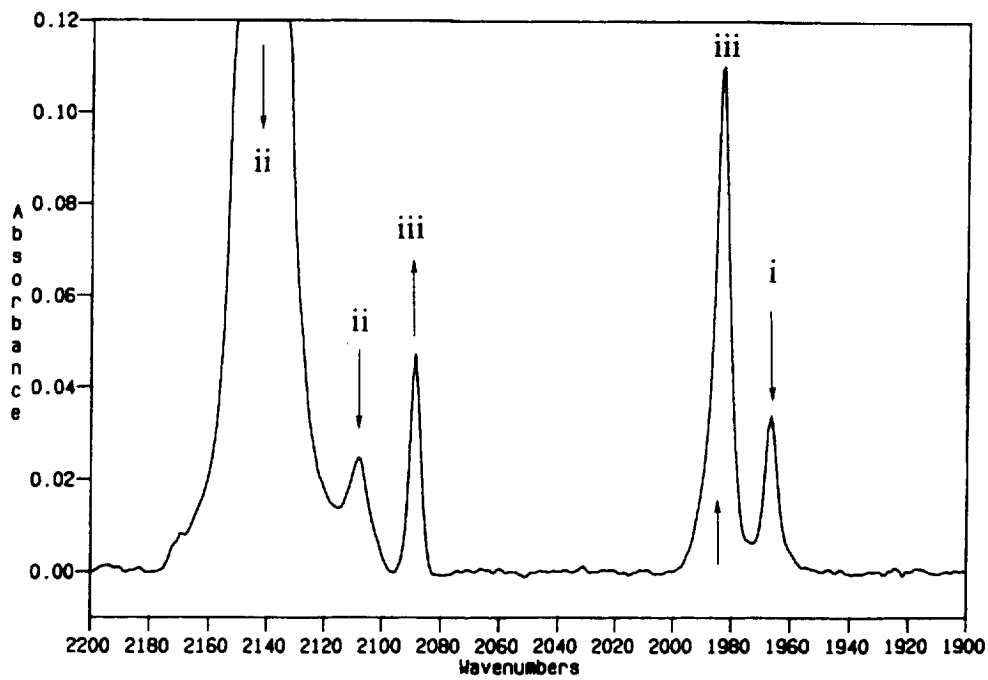
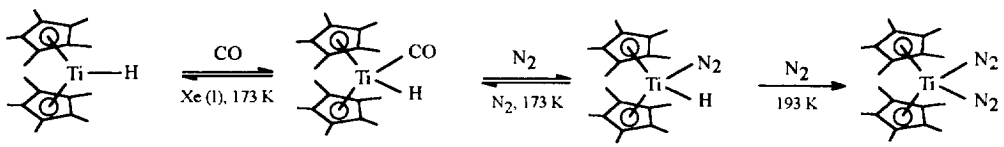
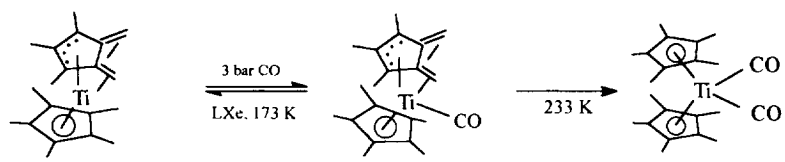


Fig. 2. IR spectral changes in the 2020–1900 cm^{-1} region of Cp^*_2TiH + 3 bar N_2 in LXe upon warming up from 173 to 243 K: (i) $Cp^*_2TiH(CO)$; (ii) $Cp^*_2TiH(N_2)$; (iii) $Cp^*_2Ti(N_2)_2$.

The first reaction step is the formation of the monocarbonyl adduct $Cp^*_2TiH(CO)$, which then disproportionates to $Cp^*_2Ti(H)_2$ (which is known to liberate dihydrogen [3]) and $Cp^*_2Ti(CO)$. Because of the large excess of N_2, CO is then replaced by this ligand to give $Cp^*_2Ti(N_2)$. It ends up forming the bis-dinitrogen complex $Cp^*_2Ti(N_2)_2$ (Eq. (2)), by picking up another equivalent of dinitrogen.



(2)



(3)

16 VE 18 VE 18 VE

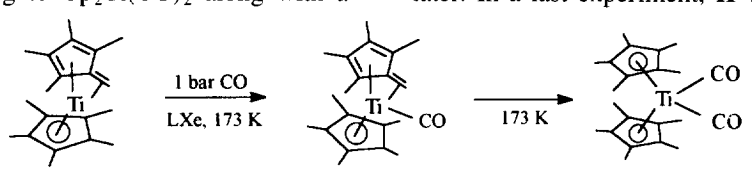
3.2. *Cp*TiCHT (II), Cp*FvTi (III), Cp*AdTi (IV)*

When **IV** was dissolved in LXe at 173 K and treated with 3 bar of CO the formation of the corresponding adduct $Cp^*AdTi(CO)$ was observed after a few seconds ($\nu^{12}CO = 2002\ cm^{-1}$). When the experiment is repeated with of ^{13}C-enriched carbon monoxide (75% ^{12}CO, 25% ^{13}CO), absorptions at 1957 (^{13}CO) and 1910 ($^{13}C^{18}O$) cm^{-1}, respectively, were obtained, in agreement with the expected wavenumber shifts of an undistorted diatomic oscillator. At 233 K, new absorptions belonging to $Cp^*_2Ti(CO)_2$ along with a simultaneous decrease of the bands of the adduct were found. At higher temperature and concentration of the dicarbonyl, CO bands of isotopomers could also be detected, while at the same time the monocarbonyl bands disappeared completely. The characteristic IR frequencies of the dicarbonyl are given in Table 2.

The formation of the dicarbonyl $Cp^*_2Ti(CO)_2$ via the thermolabile adduct $Cp^*AdTi(CO)$ is explained by a ligand exchange reaction (Eq. (3)).

A similar reaction was observed for the closely related complex **III**. With the addition of 1 bar CO at 173 K a new carbonyl absorption at 1948 cm^{-1}, assigned to $Cp^*FvTi(CO)$, was observed. This complex is very labile and decomposes, even at 173 K, into the dicarbonyl $Cp^*_2Ti(CO)_2$ (Eq. (4)).

Unfortunately, the mechanism of these intriguing ligand exchange reactions of **III** and **IV** could not be elucidated by IR spectroscopy. They are the results of further investigations which will be published later. In a last experiment, **II** was treated in LXe at

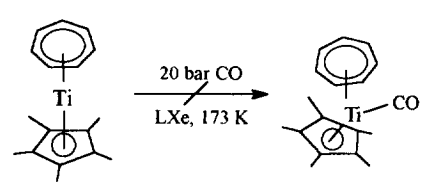


(4)

15 VE 17 VE 18 VE

Table 2
Carbonyl stetching fequencies of $Cp^*_2Ti(CO)_2$ isotopomers in LXe

Isotopomer	ν_{as} (cm^{-1})	ν_s (cm^{-1})
$Cp^*_2Ti(^{12}CO)(^{12}CO)$	1940	1860
$Cp^*_2Ti(^{13}CO)(^{12}CO)$	1924	1846
$Cp^*_2Ti(^{13}CO)(^{13}CO)$	1896	1817
$Cp^*_2Ti(^{13}C^{18}O)(^{13}C^{18}O)$	1879	1789



(5)

16 VE 18 VE

173 K with 20 bar CO, which is the maximum pressure allowable for the cell. Even under these reaction conditions no carbonyl frequencies could be observed (Eq. (5))):

This experiment underlines the different chemical nature of this 16 VE species compared to the other compounds under study.

4. Discussion

All parent compounds, except **II**, form CO adducts stable at low temperature and high pressure of CO. The complexation of CO proved to be reversible, except for $Cp^*FvTi(CO)$, which already decomposed at the temperature of 173 K (Eq. (6)).

All adducts are thermolabile and undergo secondary

$$Cp^*R'Ti(R) \underset{T\downarrow/P\uparrow}{\overset{T\uparrow/P\downarrow}{\rightleftharpoons}} Cp^*R'Ti(R)(CO) \xrightarrow{\Delta} \text{further products} \quad (6)$$

reactions. In the case of $Cp^*_2TiR(CO)$, the thermal stability varies with the CO stretching frequency according to expectations: the lower the frequency, the higher the temperature to which the intermediate can be warmed before consecutive reactions set in. The more stable the intermediate CO adduct, the stronger the π-back bonding to the CO ligand. The stability of $Cp^*_2TiO^tBu(CO)$ is a special case: it shows the lowest complex stability of all $Cp^*_2TiR(CO)$ intermediates. This can be explained in terms of two effects which strengthen each other. The O^tBu group inhibits the complex formation both *sterically* — it is very bulky — and *electronically* — the oxygen lone pair coordinates intramolecularly, so the compound may better be described as a 17 VE species (Eq. (7)).

$$\underset{15\ VE}{Cp^*_2Ti\text{-}OtBu} \longleftrightarrow \underset{17\ VE}{Cp^*_2Ti=O^tBu} \quad (7)$$

Subsequent reactions of the monocarbonyls can be divided into three reaction types:

(i) disproportionation reaction

$$Cp^*_2Ti^{III}(R)(CO) \xrightarrow{\Delta} Cp^*_2Ti^{II}(CO)_2$$

+ further products; R = H, Ph, OtBu

(ii) ligand exchange reaction

$$Cp^*(R')Ti(CO) \xrightarrow{\Delta} Cp^*_2Ti(CO)_2$$

+ further products; R′ = Fv, Ad

(iii) CO insertion into a Ti–C bond

The driving force for reactions (i) and (ii) seems to be

(1) disproportionation reaction

$$Cp^*_2Ti^{III}(R)(CO) \xrightarrow{\Delta} Cp^*_2Ti^{II}(CO)_2 + \text{further products}$$

R = H, Ph, O^tBu

(2) ligand exchange reaction

$$Cp^*(R')Ti(CO) \xrightarrow{\Delta} Cp^*_2Ti(CO)_2 + \text{further products}$$

R' = Fv, Ad

(3) CO insertion into a Ti-C bond

$$Cp^*_2Ti(R)(CO) \xrightarrow{\Delta} Cp^*_2Ti\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow{\Delta} \text{further products}$$

R = Me, Ph

the formation of $Cp^*_2Ti(CO)_2$, which is a thermodynamically favoured product. Thus the formation of this complex is the preferred reaction at low temperatures; at higher temperatures CO insertion into the Ti–C bond is also possible. The high temperature reactions, especially, are still not well understood because of the limited information provided by the IR technique.

From the N_2 experiments it can be concluded that **Ib** is a very unsaturated species. It reacts with 3 bar N_2 in LXe at 173 K to produce a high concentration of $Cp^*_2TiH(N_2)$. Because of the high quality of the IR spectra in LXe, the stretching frequency $\nu(^{14/15}N_2)$ could also be observed (intensity 1:0.007). If this N_2 molecule is end-on bonded, a split in this satellite band is expected. The observation of an unsplit band may have two causes: the N_2 molecule is side-on bonded, or the split is smaller than two wavenumbers and cannot be resolved by the spectrometer. The second reason seems more plausible since nitrogen side-on complexes are rare, but the other possibility cannot, however, be excluded. Warming up to 193 K gave rise to the formation of the bis-dinitrogen complex $Cp^*_2Ti(N_2)_2$ by disproportionation, in analogy to the CO case.

Finally, the results obtained in the two different IR cells (LXe and LT-FAIR) should be compared with regard to their spectral qualities. The best spectral results were obtained with the 30 mm LXe cell at 173 K. Advantages are the complete transparency of LXe in the IR region, negligible interactions between species and solvent and a high temperature accuracy obtained with the cell because of its solid construction. Disadvantages are the high price of high purity xenon and very weak interactions between species and solvent, which drastically limits solubility. Only covalently bonded molecular species with a dipole moment close to zero can be investigated in this solvent. In addition, the maximum temperature of the LXe cell is only 243 K, which does not allow studies at ambient temperature. Most of these disadvantages can be solved by using the LT-FAIR cell instead, which is commercially available [8]. Temperature range and solubility are often not limited, since many organic solvents are available. The construction is simpler (no overpressure) and allows free access to the reaction volume for gases and reactants in solution, so that chemistry with intermediates is possible. Nevertheless, these advantages may be compensated by the presence of IR absorption of the solvent used, which causes a drastic loss of spectral quality.

Acknowledgements

M. Tacke thanks the Deutsche Forschungsgemeinschaft for a post-doctoral fellowship and the Nederlandse organisatie voor wetenschappelijk onderzoek for a research grant.

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